Reinvestigation of the Behaviour of Benzal-anils towards the Action of Potassium Cyanide

Ibrahim I. Abd El Gawad*, Abd El-Hammid Harhash+, and Mohamad, M. M. Abou El-Zahab
Chemistry Department, Faculty of Science, Mansoura University, and +Cairo University, Giza, Egypt
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Benzal-anils, Addition Reaction, 4-Imidazolidinone, Ring Closure

Reinvestigation of the behaviour of benzal-anils (1) towards the action of potassium cyanide was found to give a mixture of 4-imidazolidinone (6) and 4-imidazolone (7). It was also obtained by benzaldehyde addition to α-arylmino-α-phenylacetanilide (7) or by condensation of benzaldehyde with α-arylmino-α-phenylacetamide (8). The partial conversion of 6 and 7 to each other was discussed.

It has been reported [1] that the reaction of benzal-anil (1) with potassium cyanide in acetic acid afford α-phenylamino-α-phenylacetanitrite (2), whereas in ethanol afford three products, two isomeric structure (3) beside an acid (4) [2]. The structure of the isomeric products 3 has been questioned by Davis and Levy [3], who assumed that the compounds were probably 5-imino-oxazolidine (5) and the 4-imidazolidinone (6a).

Recently, the reaction of salicyldiene-anils with potassium cyanide in ethanol was found to give the salicyldiene derivatives of 2-amino-3-arylamino-benzofuran [4], and not as previously reported metaxazole derivatives [5].

The above contradiction in literature [2-5] prompted us to reinvestigate the behaviour of benzal-anils (1a-c) towards the action of potassium cyanide in ethanol. On treatment benzalaniline (1a) with potassium cyanide in ethanol, only two products, of melting points comparable to those isomers previously isolated [2, 3] were obtained. The IR spectrum of the lower m.p. product agrees well with the structure 6a which showed absorption bands characteristic for C = O, and NH groups. However, the IR spectrum of the higher m.p. product showed absorption bands characteristic for C = O, and C = N groups and did not reveal NH absorption which excludes the possibility of the iminooxazolidine (5). The mass spectra of the two products showed identical fragmentation patterns and molecular ions m/e 314 and 312, respectively. The fragmentation patterns of product 7a showed molecular ion (M+), at 312) and probably it takes place via four routes.

The two products are therefore given the 4-imidazolidinone (6), and the corresponding oxidised product 4 imidazolone (7a) structures, respectively. Similarly, the benzal-anils (1b, c) afforded the imidazolidinones (6a-c) and the imidazolones (7b, e) when treated with potassium cyanide under the same conditions.
The mechanistic pathway by which 6a-e is obtained (cf. Scheme B) was confirmed by either benzaldehyde addition to a-arylamino-a-phenyl acetonitrile (2a-e) or by the condensation of benzaldehyde with a-anilino-a-phenylacetamide (8), obtained from the hydrolysis of 2.

The partial conversion of 6 into 7 is probably due to autooxidation, since 6a afforded 7a by refluxing in ethanol or by air oxidation. Moreover, reduction of 7a with sodium amalgam afforded 6a.

**Experimental**

Analytical data were determined by the Microanalytical Unit Cairo University. Infrared spectra were recorded on a SP 1000 Pye-Unicam spectrophotometer. Mass spectrum were also recorded on Varian MAT. CH-5 DF. All the melting points are uncorrected.

**4-Imidazolidinones (6a-c) and 2-imidazolin-4-ones (7a-c)**

A) Reaction of benzal anils (1) with potassium cyanide in ethanol

A mixture of benza 9

laromatic amines (1a-c) (0.2 mole), potassium cyanide (0.2 mole) in ethanol (300 ml) was heated under reflux for 2 h. The reaction mixture was cooled. The solid product that separated was collected by filtration. Recrystallisation of the product from ethanol gave 1-aryl-2,5-diphenyl-2-imidazolin-4-ones (7a-c) as colourless crystals. The results are given in Table I.

Infrared measurements showed stretching frequencies at 1720, and 1635 cm⁻¹ characteristic for C=O, and C=N groups respectively. Chilling the mother liquer in ice gave a second solid. The crystal that separated were collected by filtration, and recrystallised from ethanol to give 1-aryl-2,5-diphenyl-4-imidazolidinones (6a-c). The results are given in Table II.

Infrared measurements showed stretching frequencies at 1720, and 3350 cm⁻¹ characteristic for C=O, and NH groups respectively.

B) Reaction of a-arylamino-a-phenylacetonitriles (2a-c) with benzaldehyde

A mixture of a-arylamino-a-phenylacetonitriles (2a) [1, 6, 7] (0.1 mole), benzaldehyde (0.15 mole), and potassium hydroxide (10 g) in ethanol (500 ml) was heated under reflux for 2 h. The reaction mixture was poured into water. The solid product that

Table I. 1-Aryl-2,5-diphenyl-2-imidazolin-4-ones (7a-c).

<table>
<thead>
<tr>
<th>Compound</th>
<th>m.p. [°C]</th>
<th>Yield [%]</th>
<th>Formula (mol. wt)</th>
<th>Carbon [%] Found</th>
<th>Caled</th>
<th>Hydrogen [%] Found</th>
<th>Caled</th>
<th>Nitrogen [%] Found</th>
<th>Caled</th>
</tr>
</thead>
<tbody>
<tr>
<td>7a</td>
<td>255</td>
<td>41</td>
<td>C₂₁H₁₈N₅O         (312.38)</td>
<td>80.8</td>
<td>80.77</td>
<td>5.2</td>
<td>5.1</td>
<td>9.2</td>
<td>9.0</td>
</tr>
<tr>
<td>7b</td>
<td>244</td>
<td>38</td>
<td>C₂₂H₂₀N₅O         (326.4)</td>
<td>80.1</td>
<td>80.5</td>
<td>6.2</td>
<td>6.1</td>
<td>8.5</td>
<td>8.6</td>
</tr>
<tr>
<td>7c</td>
<td>250</td>
<td>39</td>
<td>C₂₂H₂₀N₅O         (326.4)</td>
<td>80.6</td>
<td>80.5</td>
<td>6.0</td>
<td>6.1</td>
<td>8.6</td>
<td>8.6</td>
</tr>
</tbody>
</table>

Table II. 1-Aryl-2,5-diphenyl-4-imidazolidinones (6a-c).

<table>
<thead>
<tr>
<th>Compound</th>
<th>m.p. [°C]</th>
<th>Yield [%]</th>
<th>Formula (mol. wt)</th>
<th>Carbon [%] Found</th>
<th>Caled</th>
<th>Hydrogen [%] Found</th>
<th>Caled</th>
<th>Nitrogen [%] Found</th>
<th>Caled</th>
</tr>
</thead>
<tbody>
<tr>
<td>6a</td>
<td>209</td>
<td>40</td>
<td>C₂₁H₁₈N₅O         (314.39)</td>
<td>79.7</td>
<td>80.2</td>
<td>5.9</td>
<td>5.7</td>
<td>9.0</td>
<td>8.9</td>
</tr>
<tr>
<td>6b</td>
<td>207</td>
<td>38</td>
<td>C₂₂H₂₀N₅O         (328.42)</td>
<td>80.6</td>
<td>80.48</td>
<td>6.3</td>
<td>6.1</td>
<td>8.5</td>
<td>8.5</td>
</tr>
<tr>
<td>6c</td>
<td>223</td>
<td>37</td>
<td>C₂₂H₂₀N₅O         (328.42)</td>
<td>80.3</td>
<td>80.48</td>
<td>6.1</td>
<td>6.1</td>
<td>8.2</td>
<td>8.5</td>
</tr>
</tbody>
</table>
separated was filtered and recrystallised from ethanol to give 1-aryl-2,5-diphenyl-2-imidazolin-4-ones (7a–e) as colourless crystals (cf. Table I).

The mother liquor was chilled in ice and the crystals that separated were filtered, and recrystallised from ethanol to give 1-aryl-2,5-diphenyl-4-imidazolidinones (6a–e) (cf. Table II).

**Preparation of α-anilino-α-phenylacetamide (8)**

A mixture of α-phenylamino-α-phenylacetonitrile (2a) (2 g) and concentrated sulphuric acid (50%, 20 ml) was heated to 80–90 °C, for 30 min. The reaction mixture was cooled and the solid product formed was collected. Recrystallisation from ethanol gave α-anilino-α-phenylacetamide (8); m.p. 73 °C, yield 90%.

**Analysis for C14H14N2O**

Calcd C 74.31 H 6.24,  
Found C 75.1 H 6.2.

**Action of α-anilino-α-phenylacetamide (8) with benzaldehyde**

A mixture of α-anilino-α-phenylacetamide (8) (0.01 mole), and potassium hydroxide (0.5 g) in ethanol (20 ml) was heated under reflux for 3 h. The reaction mixture was cooled and the solid product formed was collected. Recrystallisation from ethanol gave 4-imidazolidinone (6a) m.p. 209 °C, yield 83% (mixed melting point with an authentic specimen undepressed).

**Conversion from 6a to 7a**

Compound 6a (1.0 g) was heated under reflux in ethanol (30 ml) for 8 h. The reaction was cooled by filtration. Recrystallisation from ethanol gave 7a. Characterised by m.p. and m.m.p., yield 71%.

**Action of sodium amalgam 2-imidazolin-4-one (7a)**

1 g sodium amalgam was added in small portions to a suspension of 2-imidazolin-4-one (7a) (1.0 g) in ethanol (100 ml). The reaction mixture was refluxed for 2 h and set aside overnight at room temperature. The resulting solid product that separated was recrystallised from ethanol to give 1,2,5-triphenyl-4-imidazolidinone (6a) as colourless crystals (mixed melting point with an authentic specimen undepressed).